Cambridge International AS & A Level

CANDIDATE NAME	

CENTRE NUMBER			CANDIDATE NUMBER	

CHEMISTRY **9701/41**

Paper 4 A Level Structured Questions **May/June 2021**

2 hours

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

● Answer **all** questions.
● Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
● Write your name, centre number and candidate number in the boxes at the top of the page.
● Write your answer to each question in the space provided.
● Do **not** use an erasable pen or correction fluid.
● Do **not** write on any bar codes.
● You may use a calculator.
● You should show all your working, use appropriate units and use an appropriate number of significant figures.

INFORMATION

● The total mark for this paper is 100.
● The number of marks for each question or part question is shown in brackets [ ].

This document has **24** pages. Any blank pages are indicated.

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Answer **all** the questions in the spaces provided.

1 (a) The carbonates and hydroxides of Group 2 elements show similar trends in thermal stability.

Suggest and explain the variation in the trend in the thermal stability of the Group 2 hydroxides.

....

....

....

....

.... [3]

(b) Calcium hydroxide is slightly soluble in water.

(i) Write an equation to show the dissociation of calcium hydroxide, $Ca(OH)_2(s)$, in aqueous solution. Include state symbols.

.... $\rightleftharpoons$ .... [1]

(ii) Calculate the solubility, in $mol\,dm^{-3}$, of $Ca(OH)_2$.
[K_{sp}: $Ca(OH)_2$, $5.02 \times 10^{-6}\,mol^3\,dm^{-9}$]

solubility = ... $mol\,dm^{-3}$ [2]

(iii) Suggest how the solubility of $Ca(OH)_2$ in aqueous NaOH compares to its solubility in water.

Explain your reasoning.

....

....

.... [1]

[Total: 7]

2 (a) Explain why chromium complexes are coloured.

....

....

....

....

.... [4]

(b) Four different compounds can be obtained when anhydrous chromium(III) chloride reacts with water under various conditions. When samples of each compound are reacted separately with aqueous silver nitrate, different amounts of silver chloride are precipitated. The precipitation leaves the complex ions **P**, **Q**, **R** and **S** in solution.

formula of compound	moles of AgCl precipitated per mole of complex ion	complex ion	property of complex ion
$CrCl_3(H_2O)_6$	3	**P**	non-polar
$CrCl_3(H_2O)_5$	2	**Q**	polar
$CrCl_3(H_2O)_4$	1	**R**	polar
$CrCl_3(H_2O)_4$	1	**S**	non-polar

(i) Draw three-dimensional diagrams for the structures of complex ions **P**, **Q**, **R** and **S**. Include the charges for each complex ion.
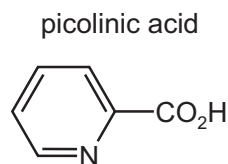
P

Cr

Q

Cr

R

Cr

S

Cr
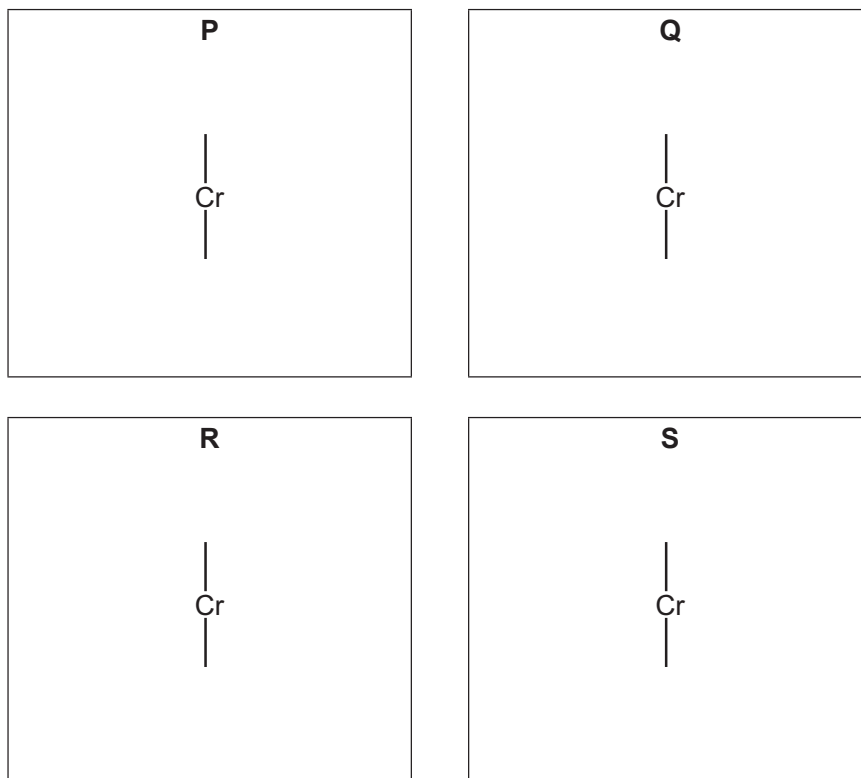
[4]

(ii) Suggest why complex ion **S** is non-polar.

....

.... [1]

(c) The structure of picolinic acid is shown.

picolinic acid

The conjugate base of picolinic acid is a bidentate ligand, **Z**.

(i) Define the term *bidentate ligand*.

....

.... [2]

(ii) Draw the structure of **Z**.

[1]

(iii) **Z** reacts with aqueous chromium(III) ions, $[Cr(H_2O)_6]^{3+}$, in a 3 : 1 ratio to form a new neutral complex.

State the coordination number and the geometry of the chromium(III) centre in the complex.

coordination number .... geometry .... [1]

(d) $(NH_4)_2Cr_2O_7$ decomposes readily on heating to form Cr_2O_3, steam and an inert colourless gas.

(i) Deduce the oxidation numbers of chromium in $(NH_4)_2Cr_2O_7$ and in Cr_2O_3.

$(NH_4)_2Cr_2O_7$ .... Cr_2O_3 .... [1]

(ii) Construct an equation for the thermal decomposition of $(NH_4)_2Cr_2O_7$.

.... [1]

[Total: 15]

3 **(a) (i)** Define the term *transition element*.

....

.... [1]

(ii) State how the melting point and density of iron compare to those of calcium.

....

.... [1]

(b) (i) Define the term *standard cell potential*, $E^{\ominus}_{cell}$.

....

....

.... [2]

(ii) Draw a fully labelled diagram of the apparatus that can be used to measure the cell potential of a cell composed of a Cu(II)/Cu electrode and an Fe(III)/Fe(II) electrode. Include all necessary reactants.

[3]

(c) The reaction between $S_2O_8^{2-}$(aq) and I^-(aq) is catalysed by adding a few drops of Fe^{3+}(aq).

(i) Use equations to show the catalytic role of Fe^{3+} in this reaction.

[2]

(ii) Fe^{3+}(aq) can oxidise I^-(aq), whereas $[Fe(CN)_6]^{3-}$(aq) cannot oxidise I^-(aq).

Use $E^\ominus$ values to explain these observations.

....

....

....

.... [2]

(d) When aqueous solutions of $S_2O_8^{2-}$ and tartrate ions are mixed the reaction proceeds very slowly. However, this reaction proceeds quickly in the presence of an Fe^{3+}(aq) catalyst.
The overall equation for this reaction is shown.

tartrate ions

$+ 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2-}$
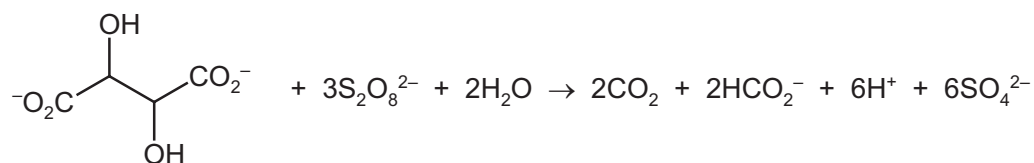
(i) Suggest why this reaction is slow without the Fe^{3+} catalyst.

....

.... [1]

(ii) Use the overall equation to deduce the half-equation for the oxidation of tartrate ions, $C_4H_4O_6^{2-}$, to carbon dioxide, CO_2, and methanoate ions, HCO_2^-.

$C_4H_4O_6^{2-}$ + ... $\rightleftharpoons$ .... [1]

(e) (i) Complete the following table to show the structures of the organic products formed when tartaric acid reacts separately with each reagent. Identify each type of reaction.

tartaric acid

$$HO_2C \overset{OH}{\underset{OH}{\diagup}} CO_2H$$
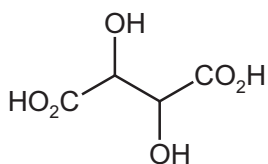
reagent	structure of organic product	type of reaction
an excess of LiAlH$_4$		
an excess of CH$_3$COCl		

[3]

(ii) Tartaric acid reacts with the amine 1-phenylethylamine, $C_6H_5CH(NH_2)CH_3$, to form an ionic salt.

Draw the structure of the salt formed in this reaction. Include the charges on the ions.

[1]

[Total: 17]

4 (a) Samples of $[Cu(H_2O)_6]^{2+}$ are reacted separately with an excess of aqueous sodium hydroxide or with an excess of aqueous ammonia.

Give the following information about these reactions.

(i) reaction 1: $[Cu(H_2O)_6]^{2+}$ with an excess of aqueous of sodium hydroxide

colour and state of the copper-containing species ....

ionic equation ....

type of reaction ....
[3]

(ii) reaction 2: $[Cu(H_2O)_6]^{2+}$ with an excess of aqueous ammonia

colour and state of the copper-containing species ....

ionic equation ....

type of reaction ....
[3]

(b) Copper(I) oxide is added to hot dilute sulfuric acid. A blue solution, **X**, and a red-brown solid, **Y**, form.

Suggest the identities of **X** and **Y**. Name the type of reaction.

X ....

Y ....

type of reaction ....
[2]

[Total: 8]

5 Dinitrogen pentoxide, N_2O_5, is dissolved in an inert solvent (solv) and the rate of decomposition of N_2O_5 is investigated. This reaction produces nitrogen dioxide, which remains in solution, and oxygen gas.
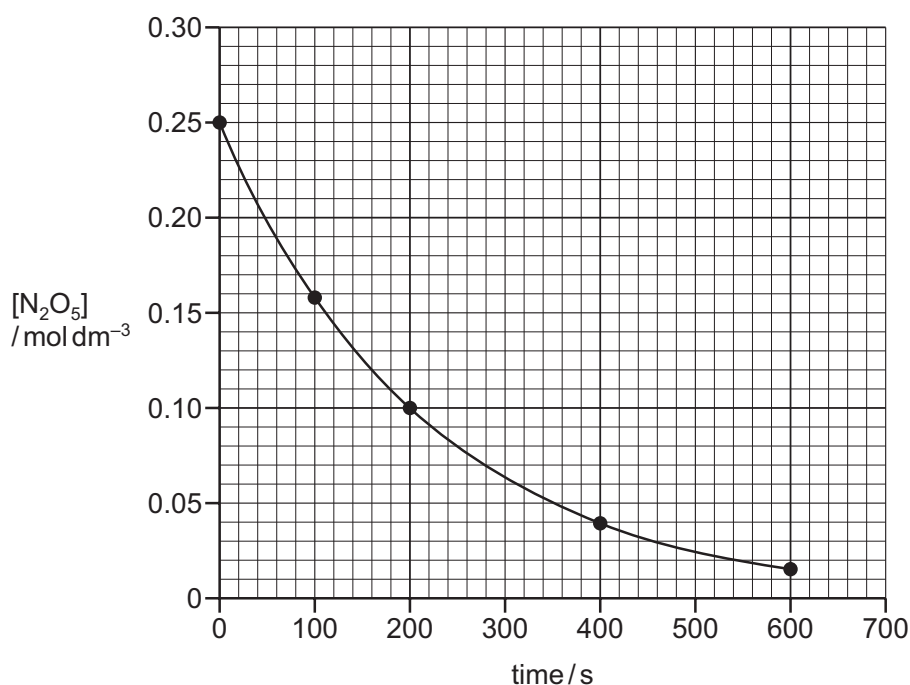
$$N_2O_5(solv) \rightarrow 2NO_2(solv) + \tfrac{1}{2}O_2(g)$$

(a) Suggest what measurements could be used to follow the rate of this reaction from the given information.

....

.... [1]

(b) In a separate experiment, the rate of the decomposition of $N_2O_5(g)$ is investigated.

$$N_2O_5(g) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

The graph shows the results obtained.

The reaction is first order with respect to N_2O_5. This can be confirmed from the graph using half-lives.

(i) Explain the term *half-life of a reaction*.

....

.... [1]

(ii) Determine the half-life of this reaction. Show your working on the graph.

half-life = ... s [1]

(iii) Suggest the effect on the half-life of this reaction if the initial concentration of N_2O_5 is halved.

.... [1]

(c) (i) Use the graph in **5(b)** to determine the rate of reaction at 200 s. Show your working.

rate = ...

units = ...
[2]

The rate equation for this reaction is shown.

$$\text{rate} = k[N_2O_5]$$

(ii) Use your answer to **(c)(i)** to calculate the value of the rate constant, k, for this reaction and state its units.

k = ... units .... [1]

(d) Nitrogen dioxide reacts with ozone, O_3, as shown.

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$
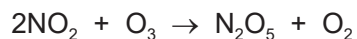
The rate equation for this reaction is rate = $k[NO_2][O_3]$.

Suggest a possible two-step mechanism for this reaction.

....

.... [2]

[Total: 9]

6 **(a)** Compare and explain the relative acidities of butanoic acid, ethanol, ethanoic acid and water.

.... > .... > .... > ....

    most acidic   least acidic

....

....

....

....

....

.... [4]

(b) Three carboxylic acids, methanoic acid, HCO_2H, ethanedioic acid, HO_2CCO_2H, and butanedioic acid, $HO_2CCH_2CH_2CO_2H$, are compared. Two tests were carried out on separate samples of each organic acid, as shown.

The following results were obtained. ✓ = observed change ✗ = no observed reaction

test	reagents and conditions	HCO_2H	HO_2CCO_2H	$HO_2CCH_2CH_2CO_2H$	observed change
1		✓	✗	✗	
2		✓	✓	✗	

(i) Complete the table with the reagents and conditions and the observed change for a positive test.
Assume these organic acids all have a similar acid strength. [3]

(ii) Each compound, HCO_2H, HO_2CCO_2H and $HO_2CCH_2CH_2CO_2H$, is dissolved seperately in $CDCl_3$. Proton (^1H) NMR and carbon-13 (^{13}C) NMR spectra are then obtained.

Complete the table.

compound	number of peaks in proton NMR	number of peaks in carbon-13 NMR
HCO_2H		
HO_2CCO_2H		
$HO_2CCH_2CH_2CO_2H$		

[2]

(iii) The proton NMR spectrum of HCO_2H in D_2O is obtained.

Describe and explain the difference observed between this spectrum and the proton NMR spectrum of HCO_2H in **(b)(ii)**.

....

....

.... [1]

(c) 1,4-dibromobutane, $Br(CH_2)_4Br$, is used in the synthesis of the dicarboxylic acid **J** and diamine **K** as shown.

$$BrCH_2CH_2CH_2CH_2Br$$

step 1   step 3

G	**H**

step 2   step 4

J	**K**
$HO_2CCH_2CH_2CO_2H$	$H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2$
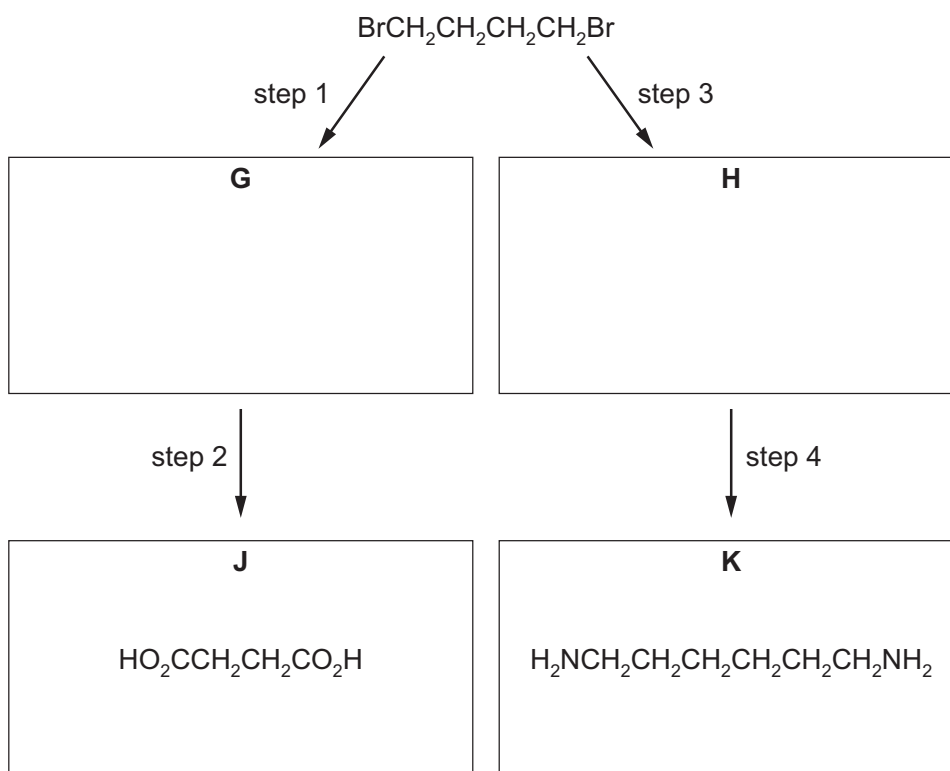
(i) Draw the structures of **G** and **H** in the boxes. [2]

(ii) Suggest reagents and conditions for each of steps 1 to 4.

step 1 ....

step 2 ....

step 3 ....

step 4 ....
[4]

(d) Polyamide **L** can be synthesised from dicarboxylic acid **J**, $HO_2C(CH_2)_2CO_2H$, and diamine **K**, $H_2N(CH_2)_6NH_2$.

Draw the repeat unit of the polymer formed in the box. Any functional groups should be shown displayed.

polyamide **L**
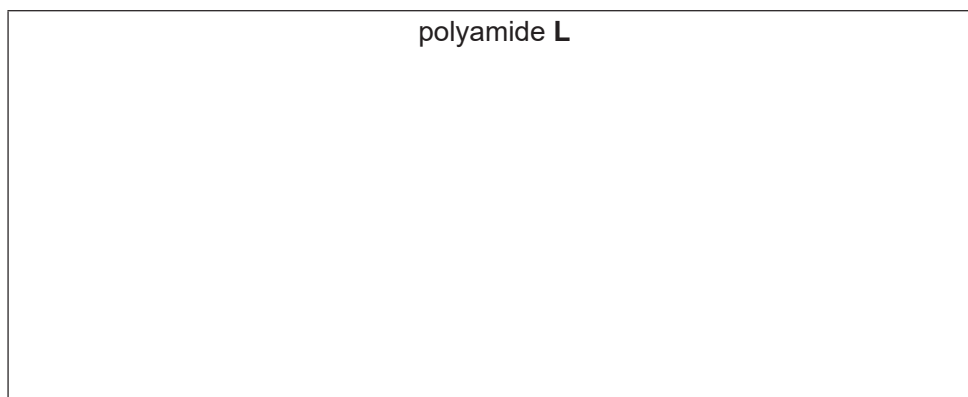
[2]

[Total: 18]

7 **(a)** 3-aminobenzoic acid can be synthesised from methylbenzene in three steps.

methylbenzene

3-aminobenzoic acid

CO$_2$H

NH$_2$
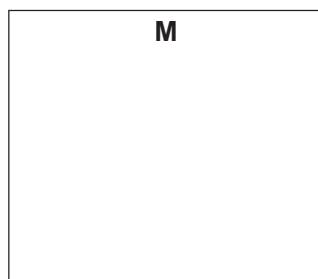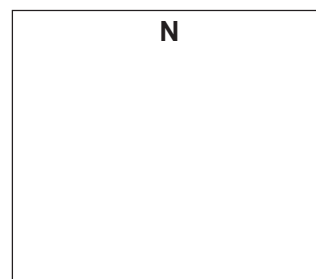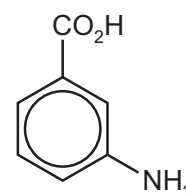
(i) Draw the structures of **M** and **N** in the boxes. [2]

(ii) Suggest reagents and conditions for each step of the synthesis.

step 1 ....

step 2 ....

step 3 ....

[3]

(b) A mixture of serine, $HOCH_2CH(NH_2)CO_2H$, and lysine, $H_2N(CH_2)_4CH(NH_2)CO_2H$, reacts to form several different products.

(i) Draw the structures of the two structural isomers with the molecular formula $C_6H_{12}N_2O_5$ that could be present in the product mixture.

The functional group formed in each case should be displayed.

[3]

(ii) Predict the number of different structural isomers with the molecular formula $C_9H_{19}N_3O_4$ that could be present in the product mixture.

molecular formula	number of structural isomers formed
$C_9H_{19}N_3O_4$	

[1]

(c) Glutathione is a naturally occurring compound found in plants.

glutathione
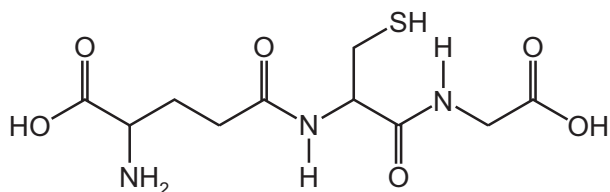
(i) On the diagram of glutathione, label each chiral centre with an asterisk (*). [1]

(ii) Draw the structures of the three products formed after complete acid hydrolysis of glutathione. Assume the thiol group, –SH, does not react.
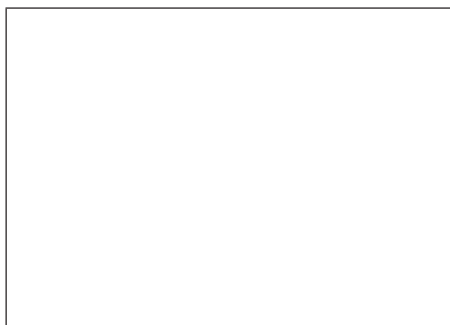
[2]

(iii) Glutathione is soluble in water.

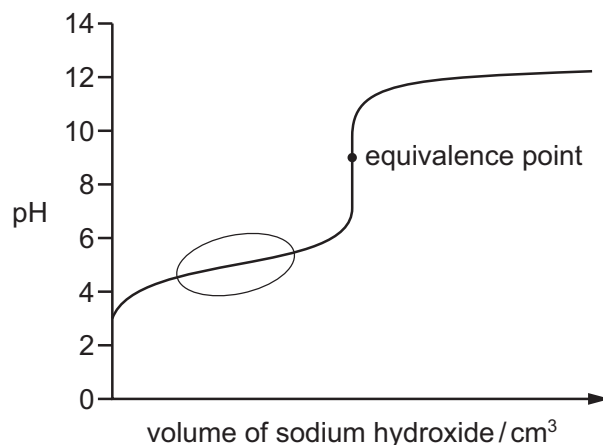By referring to the structure of glutathione, explain why glutathione is soluble in water.

....

....

.... [1]

[Total: 13]

8 **(a)** The sketch graph for the titration of ethanoic acid, CH_3CO_2H, with sodium hydroxide is shown.

(i) In the region circled on the graph, identify the **two** organic species that are present in the solution. Explain why the pH of the mixture only changes slowly and gradually in this region when sodium hydroxide is being added.

two species present ....

....

....

....

.... [3]

(ii) The equivalence point in this acid-base titration is where the two solutions have been mixed in exactly equal molar proportion.

Suggest why the pH is greater than 7 at the equivalence point in this titration.

....

....

....

.... [1]

(b) An impure sample of ammonium vanadate(V), NH_4VO_3, with mass 0.150g, is dissolved in an excess of dilute acid.

In this solution all vanadium is present as VO_2^+ ions. An excess of zinc powder is added to the solution and all the VO_2^+ ions are reduced to V^{2+} ions. The mixture is filtered to remove any remaining zinc powder.

$$VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+} + 2H_2O$$

When the resulting solution is titrated, 20.10 cm³ of 0.0250 mol dm⁻³ acidified MnO_4^- oxidises all V^{2+} ions back to VO_2^+ ions.

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

Calculate the percentage by mass of NH_4VO_3 in the 0.150g impure sample of NH_4VO_3.

Give your answer to **three** significant figures.

[M_r: NH_4VO_3, 116.9]

percentage by mass of NH_4VO_3 = ... % [3]

[Total: 7]

9 The carbon-13 (^{13}C) NMR spectrum of compound **A**, $C_8H_8O_2$, contains six peaks.

Compound **A** reacts with an excess of bromine water to give compound **B**, $C_8H_6Br_2O_2$.

Compound **A** reacts with alkaline aqueous iodine to form a yellow precipitate **C** and compound **D**.

Compound **D** reacts with PCl_5 to form compound **E**, $C_7H_5O_2Cl$.

Compound **E** reacts with propan-2-ol to form compound **F**.

Draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F** in the boxes.

A $C_8H_8O_2$		**C** yellow ppt.	**D**

alkaline I_2(aq)

+

Br_2(aq)

PCl_5

B $C_8H_6Br_2O_2$	**E** $C_7H_5O_2Cl$

propan-2-ol

F

[6]

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